

High Throughput, Solid Phase Extraction and Concentration of PFAS/PFOS in Waste Water Using EPA Method 533 and 537.1

Fluid Management Systems
Billerica, MA USA



Introduction

- Perfluoralkylated compounds contain a perfluorinated or polyfluorinated carbon chain moiety such as $\text{F}(\text{CF}_2)_n\text{-}$ or $\text{F}(\text{CF}_2)_n\text{-(C}_2\text{H}_4)_n\text{-}$.
- These make up a large group of persistent chemicals (POPs) used in industrial processes and consumer applications:
 - Stain-Resistant Coatings for textiles and carpets
 - Grease-Proof Coatings for paper products approved for food contact
 - Firefighting Foams
 - Mining and Oil Well Surfactants
 - Floor Polishes
 - Insecticide formulations

Origin

- **Industrial Sites**
- **Airport Fire Training Areas**
- **Wastewater Treatment Facilities**
- **Widespread use for over 60 years**
- **Very resistant to degradation**
- **Ubiquitous Compound in the Environment**



Global Health concerns

- **Human exposure is linked to adverse effects**
 - Developmental issues in off-spring
 - Cancer
 - Immune system suppression
 - Endocrine disruption
 - Elevated levels of Cholesterol
 - Obesity



Source concerns

- **Many water sources worldwide are found to be contaminated.**
- **Two compounds most studied:**
 - **Perfluorooctane sulphonate (PFOS)**
 - **Perfluorooctanoic acid (PFOA)**
- **Millions have been exposed through Drinking water supplies in the US and exceed the lifetime advisory of 70ng/L for these compounds**

Regulation

- **PFOS is now subject to varying but increasing levels of control in several countries.**
- **PFOA, also a widespread contaminant but with a far lower bioaccumulation potential, is still under evaluation.**



The Analysis of PFCs

- Tens of Thousands of Samples are now being analyzed and more areas of concern are starting to be analyzed for PFAS/PFOS
 - Drinking Water
 - Waste Water
 - Human Serum
 - Biota
 - Soils



Challenges in the Analysis of PFCs

- The Analytical Systems are expensive
 - UPLC/MS systems
 - Require expertise in a new technology
- Manual Sample Prep processes
 - Inconsistent results
 - Elevated Background issues
 - Labor intensive
 - Extraction can take up to 2 hours
 - Dirty samples
 - Concentration can take up to 2 hours

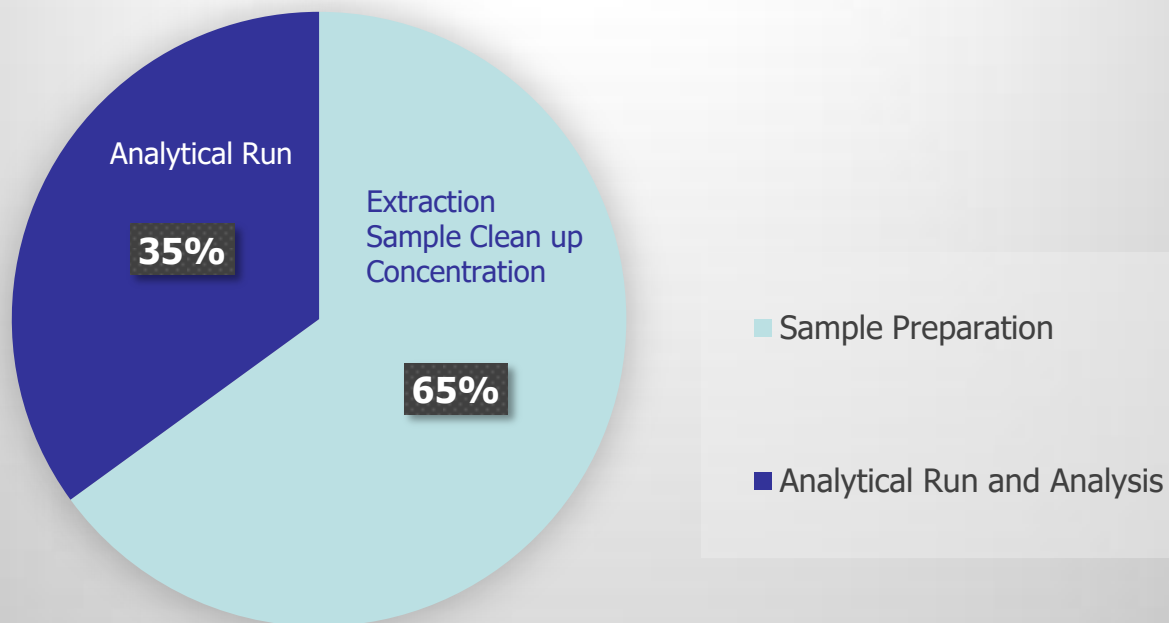
Optimizing the PFC Analysis Workflow

- **Automate the Sample Prep Workflow**
 - Automate the Solid Phase Extraction Step
 - Automate the Concentration/Evaporation Step
- **Automated, Semi Automated SPE extractions and Concentration**
 - Reduces Human Error
 - Reduces Outside contamination
 - Reduces Solvent Usage
 - Reduces Labor
- **Use SPE solutions to deliver consistent, reproducible results**



Laboratory Workflow Breakdown

Sample Prep versus Analytical in Time



Comparison of Manual SPE vs. Automated SPE Methods

Manual

Open to laboratory background

Uses >60mls solvent

Filtration process

No emulsions formed

Wide Selectivity (adsorbent)

Requires water removal

Labor intensive requires monitoring

Automated SPE

Closed system

Uses <60mls solvent

Filtration process

No emulsions formed

Wide Selectivity (adsorbent)

In-line water removal

Fast and Unattended

Comparison of Manual SPE vs. Automated SPE Methods

Manual SPE

Separates Aqueous and Organic Waste

<60mls solvent evaporate

Run times are ~ 45 minutes

Technician Time 25 minutes

Physical transfer and Concentration steps

Concentration steps 45 minutes

Automated/Semi Auto SPE

Separates Aqueous and Organic Waste

<60mls solvent to evaporate

Run times are ~ 35 minutes or less

Technician time 5 minutes

Automatic and Direct to Concentration
delivery and completion

Concentration step 45 minutes ready for
injection



Reasons for Semi-Automated SPE

- **Reduced solvent**
- **Reduced Actions**
- **Simplified procedures**
- **Semi-Automated versus Manual protocols = Reproducibility**
- **Increased Sample Throughput**
- **Low cost compared to Automated solutions**

Determining Factors

- **Ability to load samples by vacuum consistently.**
- **Ability to dry cartridges by both vacuum and positive gas pressure (N2 or CO2).**
- **Easily handle a wide variety of cartridge designs and sizes without cumbersome modifications.**
- **Simple Sample delivery**
- **Bottle Rinse**

Automated Solid Phase Extraction front end for LC/MS



EconoTrace® PFC



TurboTrace® PFC



TurboTrace®
Parallel
Sequential



Automated Concentration for PFAs

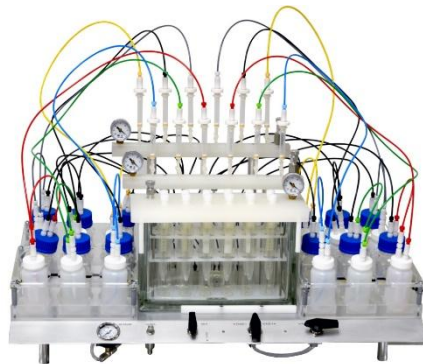
- SuperVap PFC
 - 24 positions
 - 15ml Conical vials



Semi-Automated Solid Phase Extraction front end for GC/MS and LC/MS



EZSPE



EZPFC



Sample Analysis Work Flow

Automated Sample Prep Time

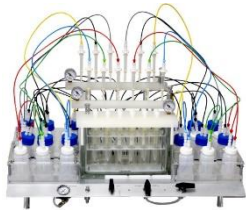
= 80 Minutes



Solid Phase Extraction
35 Minutes



Concentration
45 Minutes



Solid Phase Extraction
35 Minutes



Semi Automated Sample Prep Time

= 80 Minutes



Objective for Semi Automation

- **Use as many features as possible from the Automated systems and implement them into a Semi automated platform**
- **Develop as many SPE procedures for the testing lab using a single extraction platform.**
- **Minimize manual steps to lessen error and maximize limited man hours**

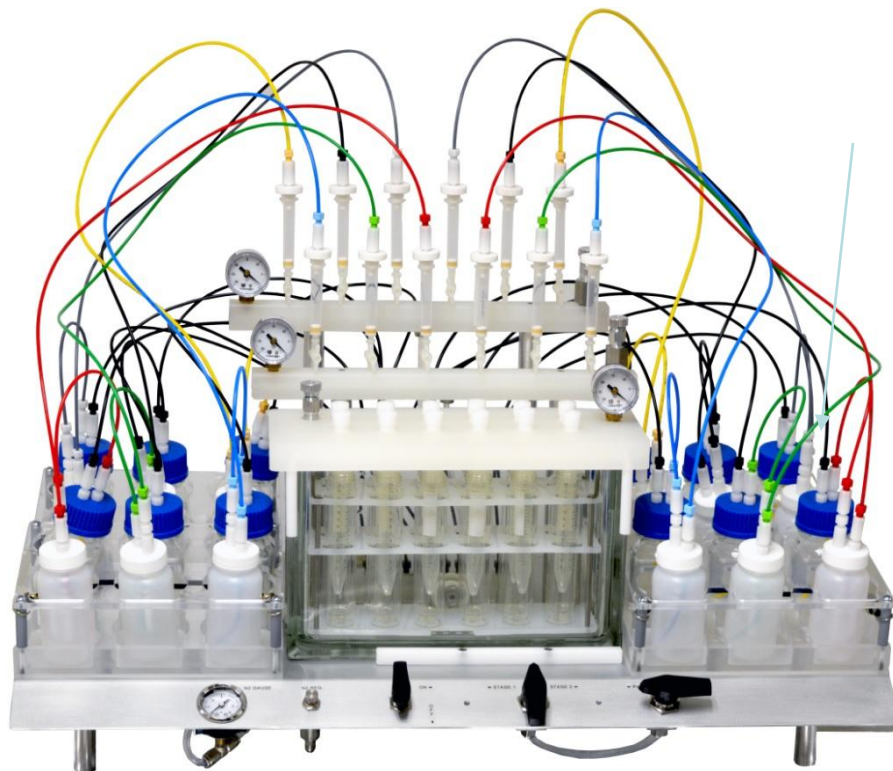
Goal

- **Self Installable**
 - Unpacking and Installation/training video
- **Easy to Operate**
 - No Computers or Electronics to fail or maintain
- **Semi - Automated**
 - Hyphenates the entire Solid Phase Extraction Process – Extraction, Bottle Rinse, Inline Drying and Optional Direct to GC Vial Concentration
- **Fast**
 - The fastest sample processing available for SPE
 - Run up to six samples simultaneously
 - Vacuum for fast loading of large volume samples
 - Unattended Sample loading walkaway time
- **Closed system**
 - Eliminate potential outside contamination

Goal

- **Efficient**
 - Uses all SPE cartridge sizes
 - Dedicated manifold for cartridge conditioning and sample loading
 - Dedicated manifold for extraction and extracts
 - Separates Organic from Aqueous waste
 - Vacuum cartridge drying, Nitrogen cartridge drying or combined
 - Automated Bottle Rinse and Elution
 - Inline Extract Drying
 - Small number of components to clean
- **Low to No Capital Expense**





EZPFC 12 sample

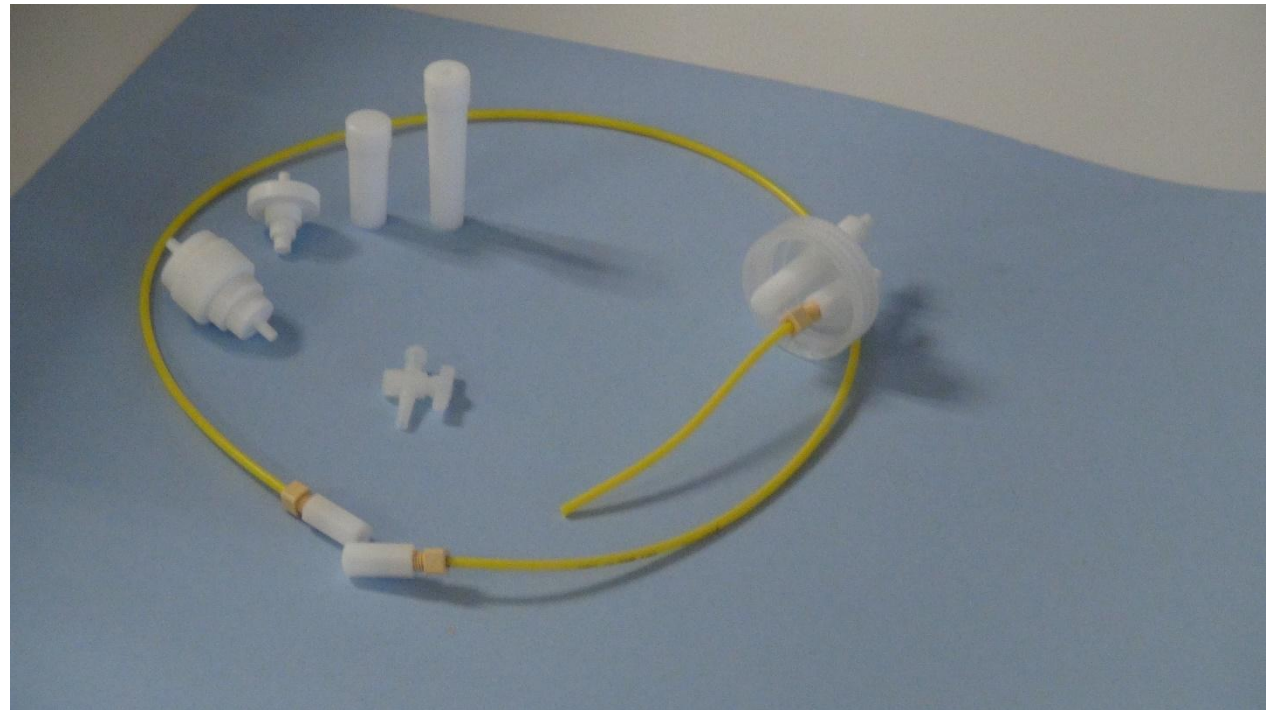
System Components

No Teflon

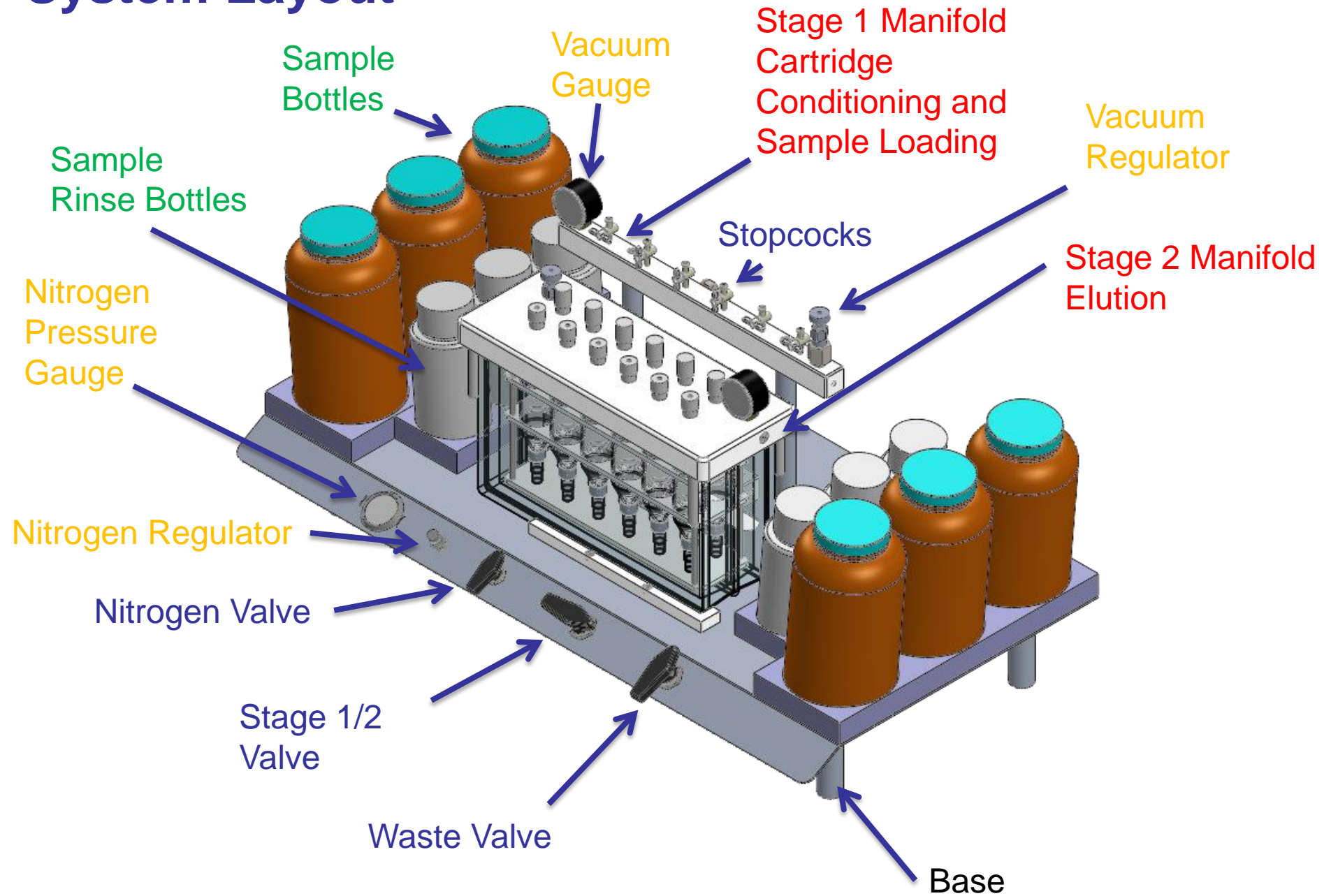
**Tubing - High Density
Polyethylene**

Fittings – Delrin

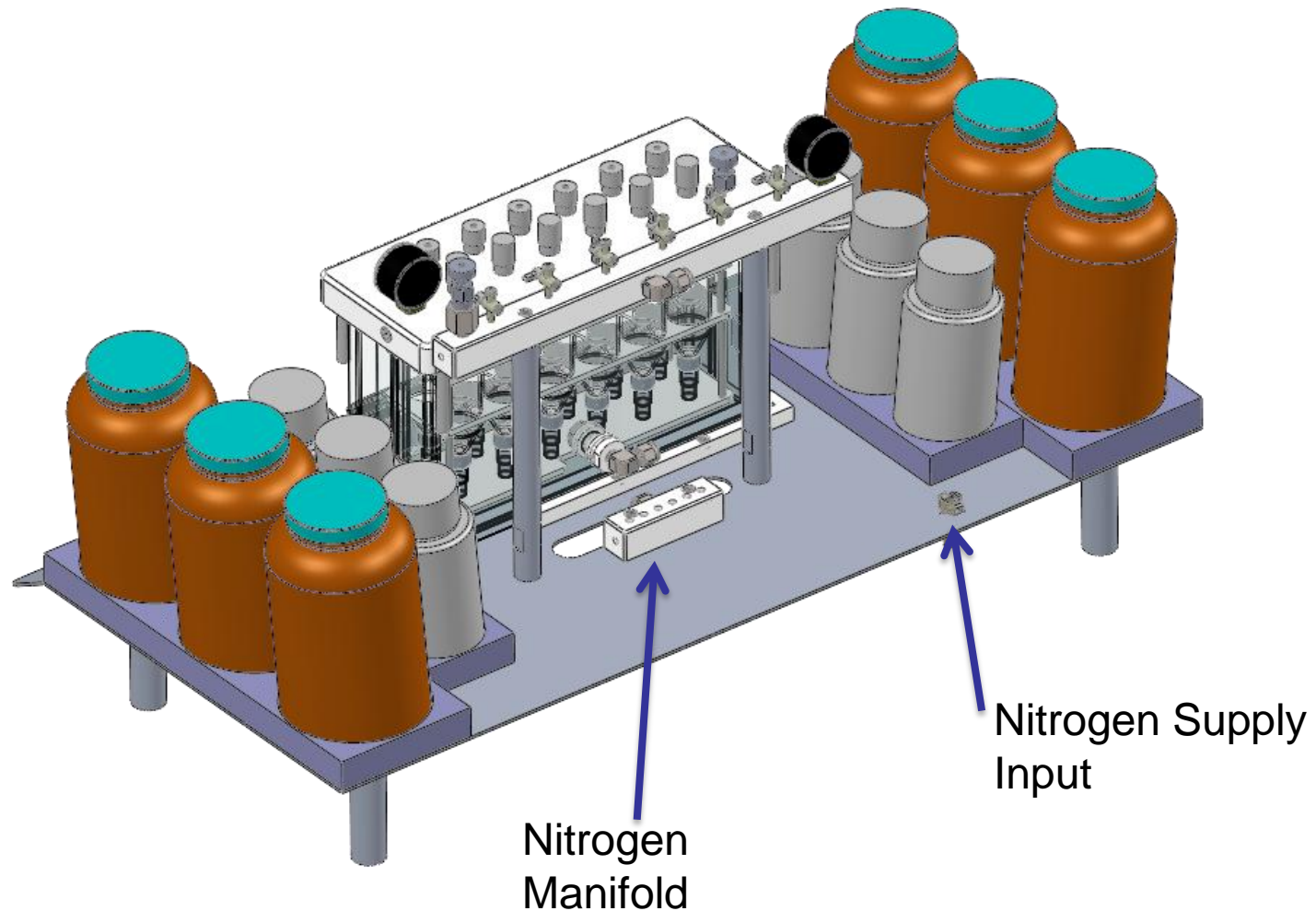
**Cartridge Adapters –
Medical Grade
Polypropylene**



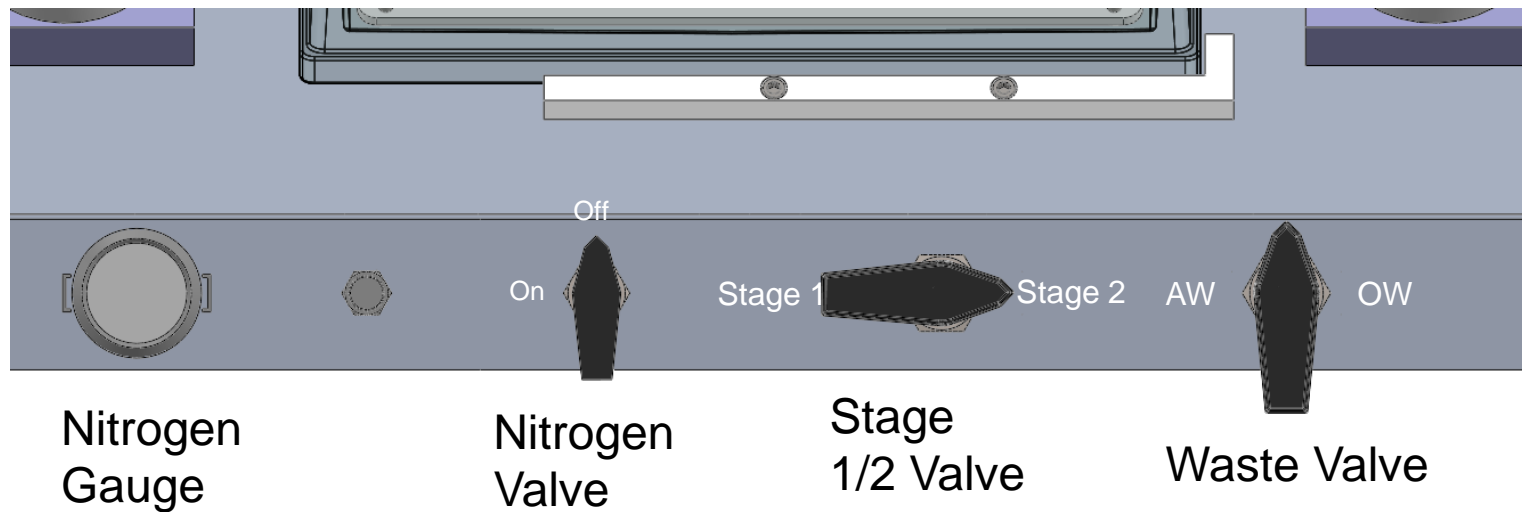
System Layout



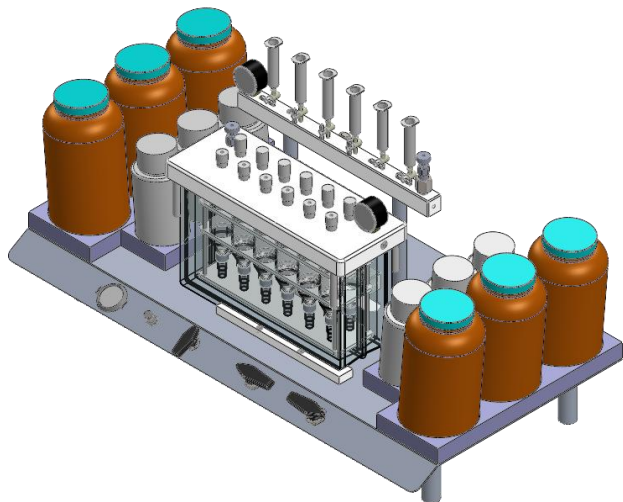
Nitrogen for Bottle Rinse and Cartridge Drying



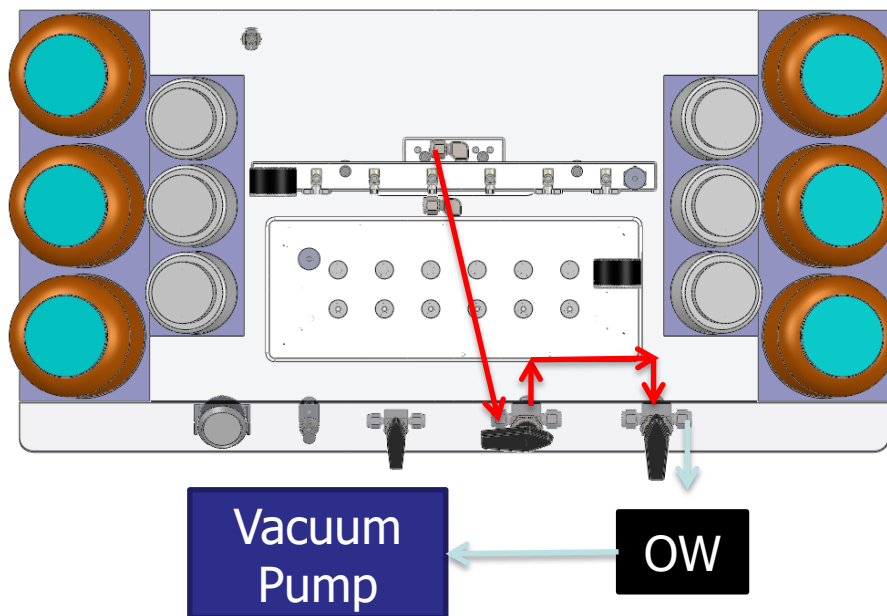
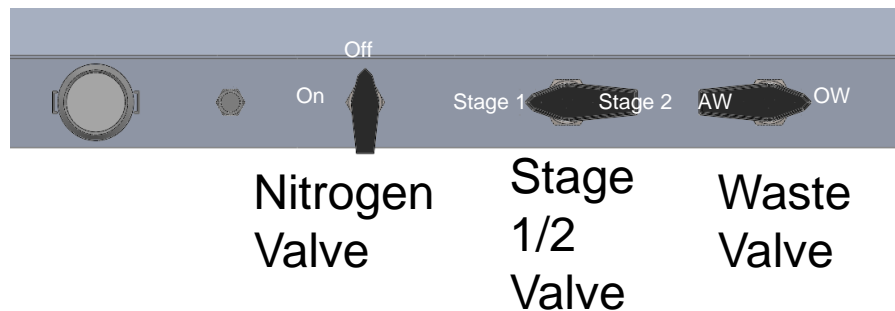
Control Valve Layout



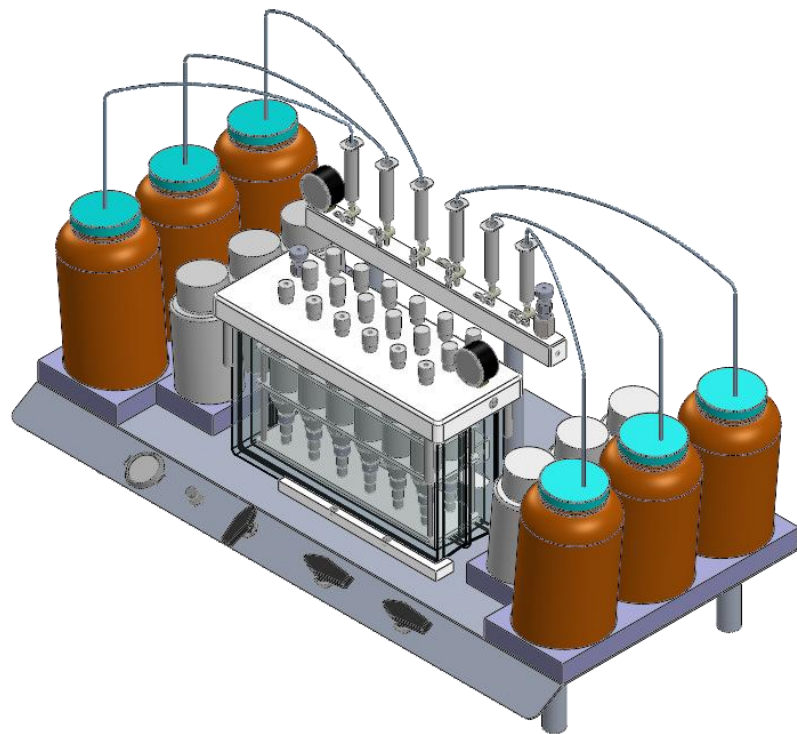
Cartridge Conditioning (Stage 1, Organic Waste)



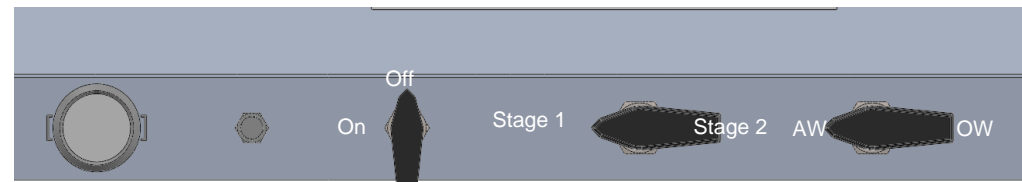
Flow
Path



Sample Loading (Stage 1, Aqueous Waste)



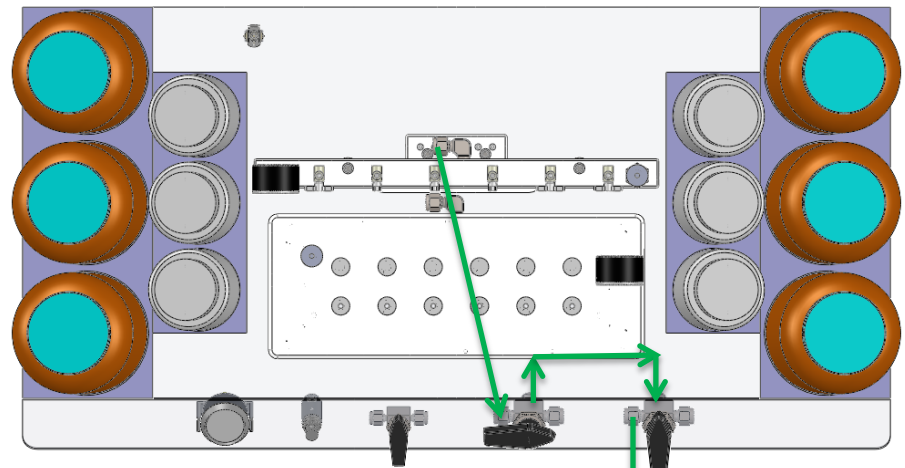
Flow
Path



Nitrogen
Valve

Stage
1/2
Valve

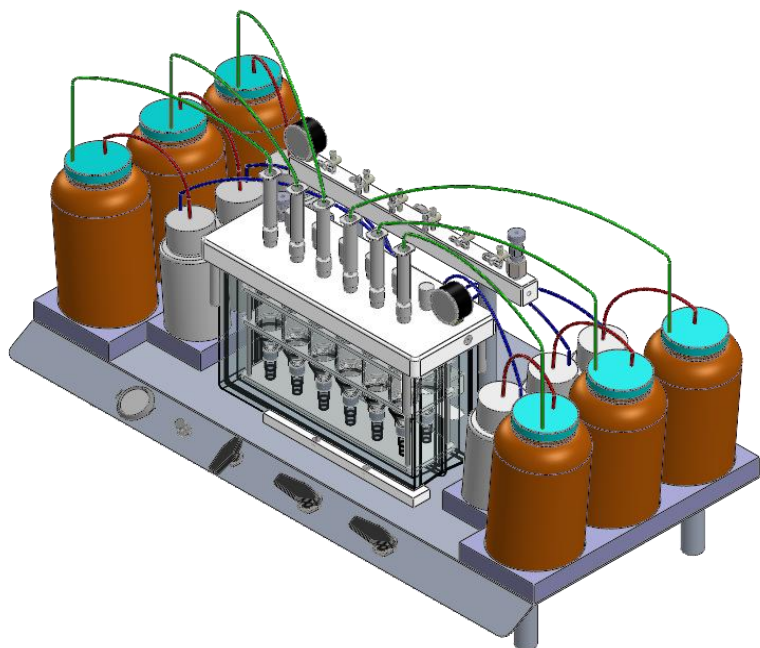
Waste
Valve



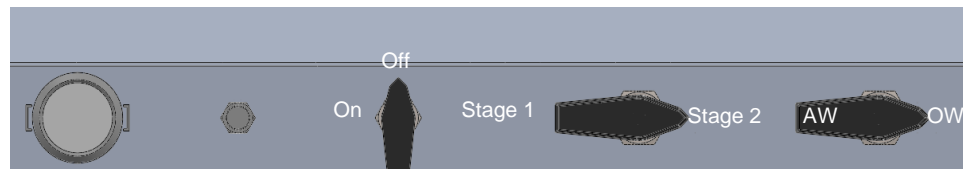
Vacuum
Pump

AW

Sample Bottle Rinse (Stage 1)



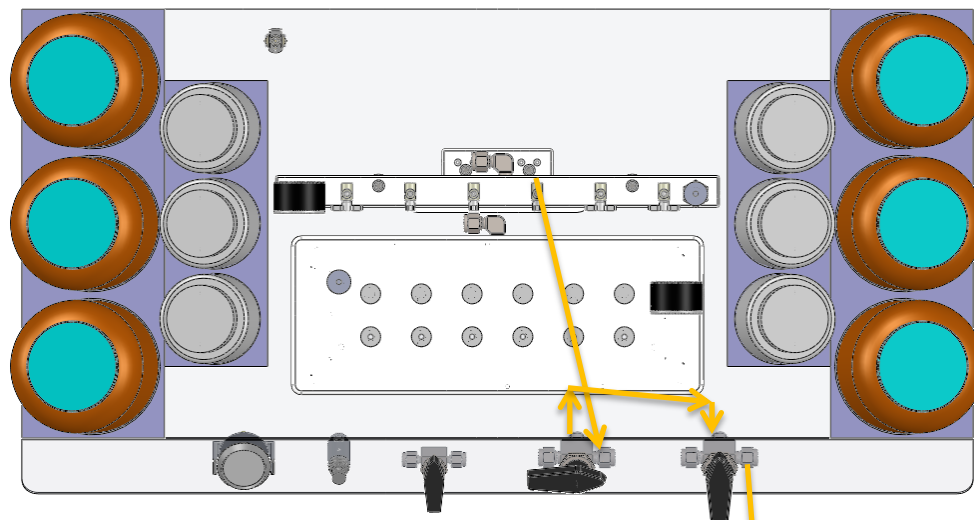
Flow
Path



Nitrogen
Valve

Stage
1/2
Valve

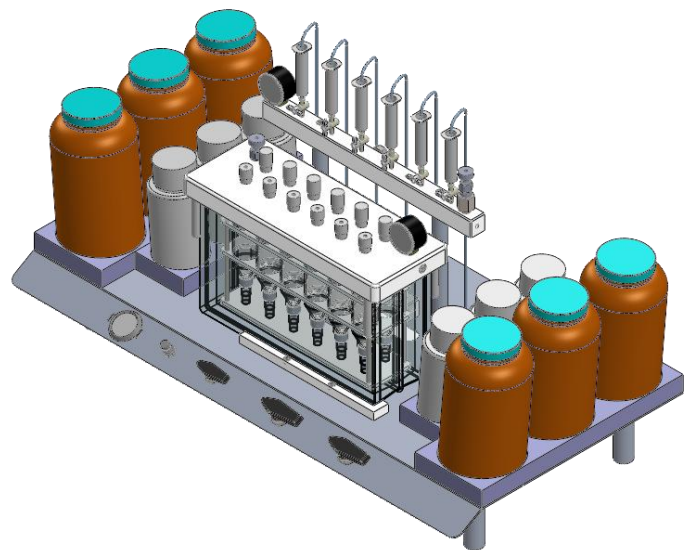
Waste
Valve



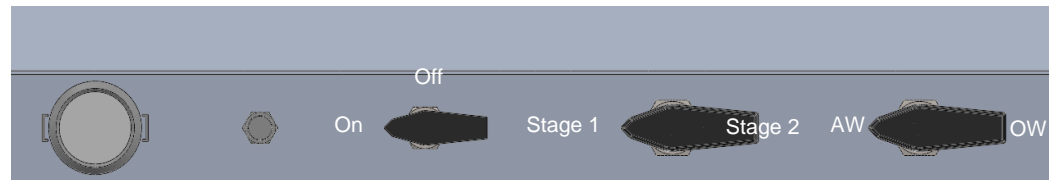
Vacuum
Pump

OW

Cartridge Drying- Nitrogen/Vacuum



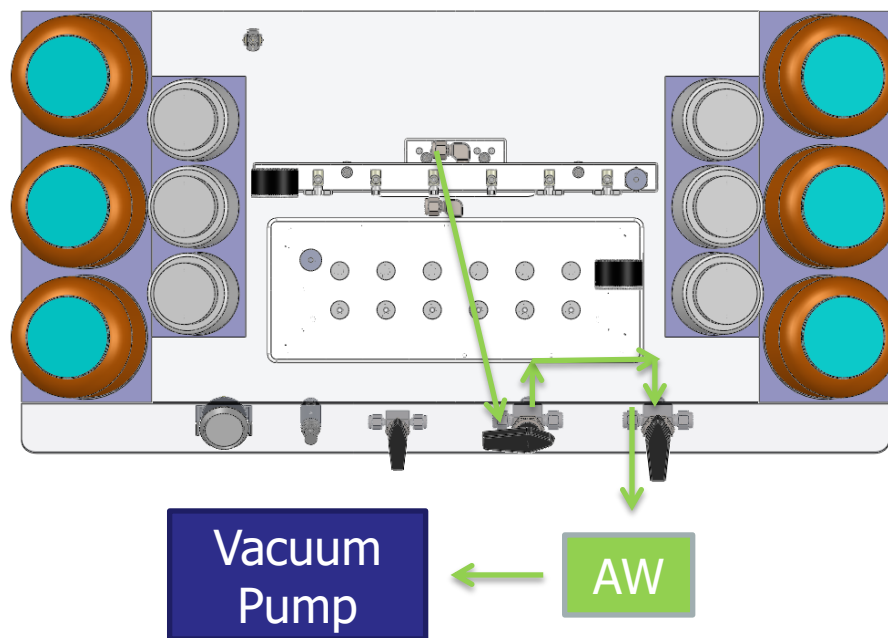
Flow
Path



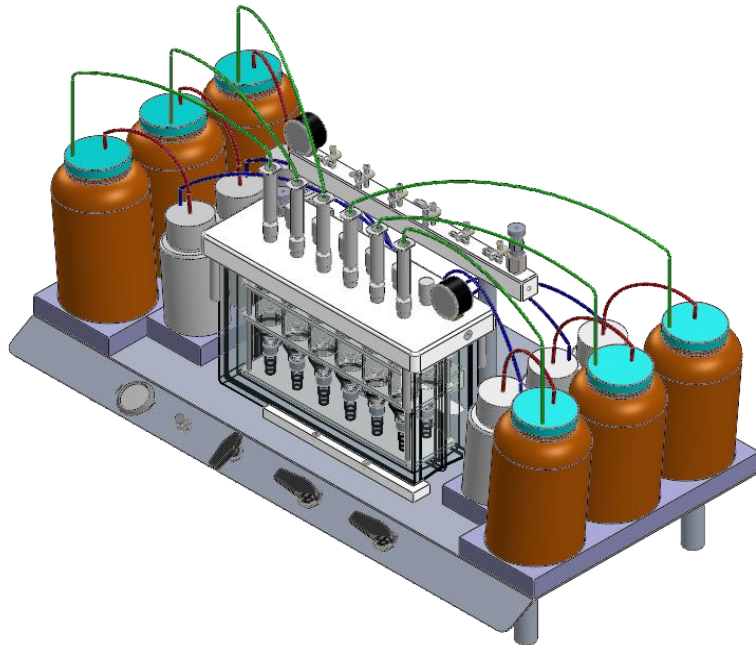
Nitrogen
Valve

Stage
1/2
Valve

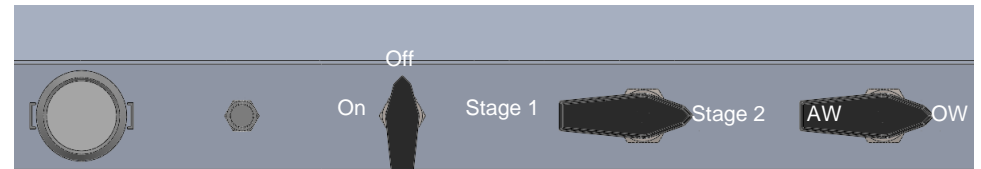
Waste
Valve



Sample Elution (Stage 2)



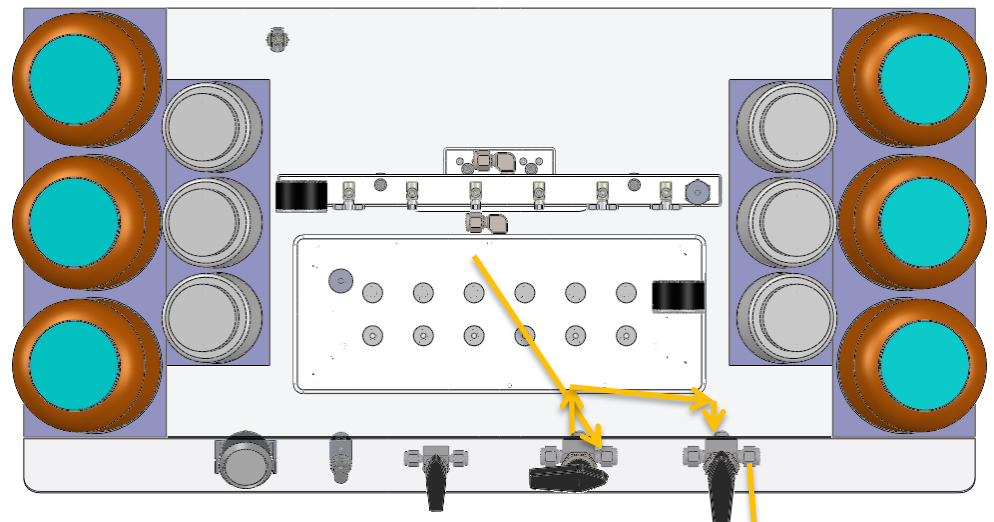
Flow
Path



Nitrogen
Valve

Stage
1/2
Valve

Waste
Valve



Vacuum
Pump

OW

PFAs Methods

- EPA 537.1
- EPA 537 v1.1
- EPA 533
- EPA 8327 with 3512: PFAS in drinking, surface, wastewater 24 compounds; no SPE; mixing 1:1 with solvent and add standards (isotope dilution); filtration; LC/MS/MS
- EPA 8327 also for solids but not specified yet how (method not finalized)



PFAs Methods

- ASTM 7968 is for 21 PFAS mostly sand and soil, solvent extraction and filtration, LC/MS
- ASTM 7979 similar to EPA 8327
- ISO 25101: 2009 this is SPE method with WAX cartridge for non-particulate or low-grade particulate water samples
- DOD QSM 5.3: PFAS in non-drinking water with SPE and isotope dilution, LC/MS/MS



Automated Concentration for PFAs

- SuperVap PFC
 - 24 positions
 - 15ml Conical vials
 - Timed Endpoint



Concentration Functionality

- **Self Installable**
 - Video unpacking, installation and training video
- **Preprogrammed with most common temperature settings**
- **6 (250mL) and 12 (50mL) position models for extractions, direct-to-vial connections**
- **Dry bath heating element**
- **Time based endpoint**
- **Savable temperature log**



Can this Handle Dirty Samples?

Typical Cartridge can have problems!

- **6ml 500mg DVB**
 - Doesn't do well
 - Frit Surface Area is too small

Yes, A Cartridge will work

- **25ml 500mg DVB cartridge**
 - Does well
 - 3X the Frit Surface Area



Delrin Plastic Wool

- Irregular random stranding
- Slows Particles to the Uniform Frit
- Prevents Clogging



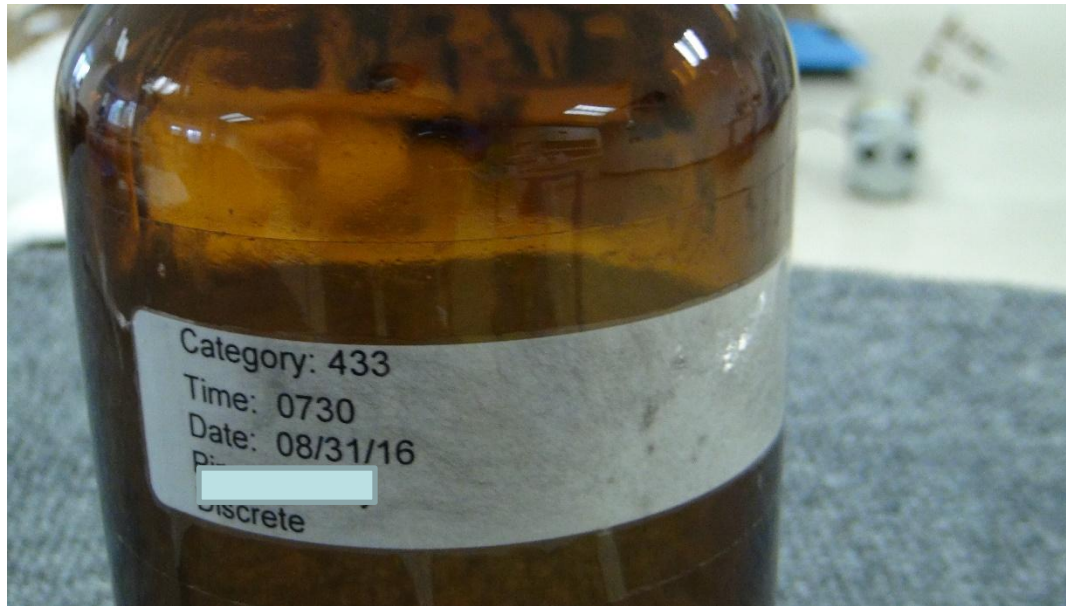
Prepping the 6ml Cartridge with Plastic Filtration Wool

6ml 500mg DVB cartridge with Plastic wool

- Take a little and push it into the barrel of the syringe until it touches the cartridge Frit
- The Sample will not clog, it will take longer to process



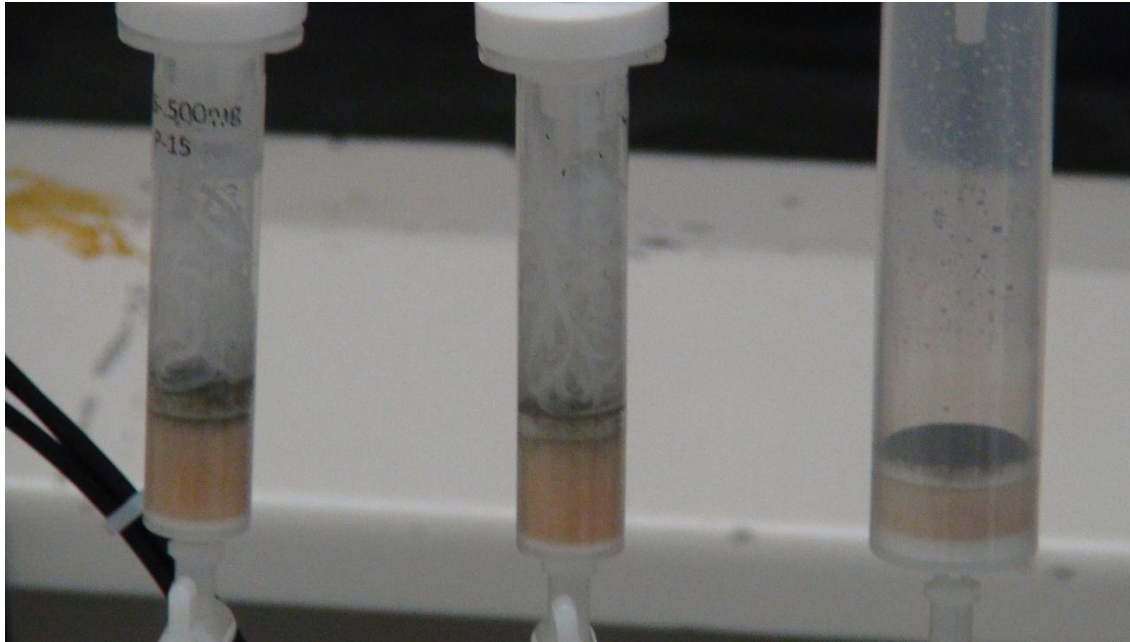
Dirty Sample from a Customer



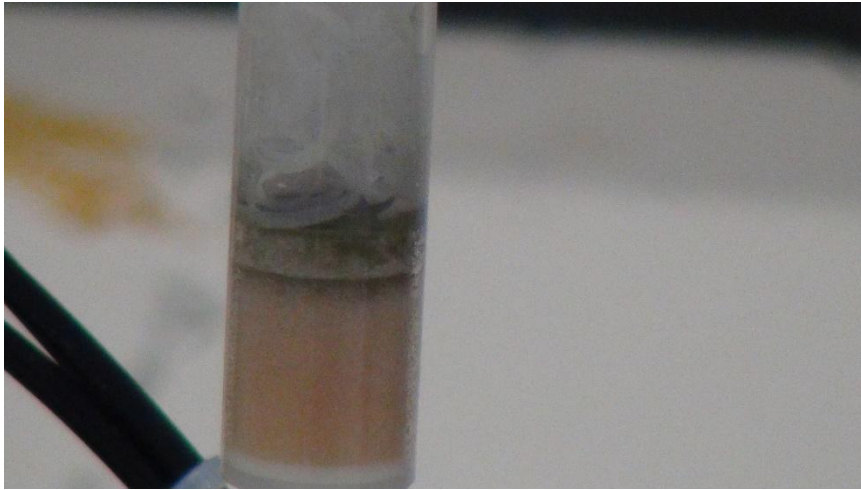
Industrial 433 Matrix 250ml



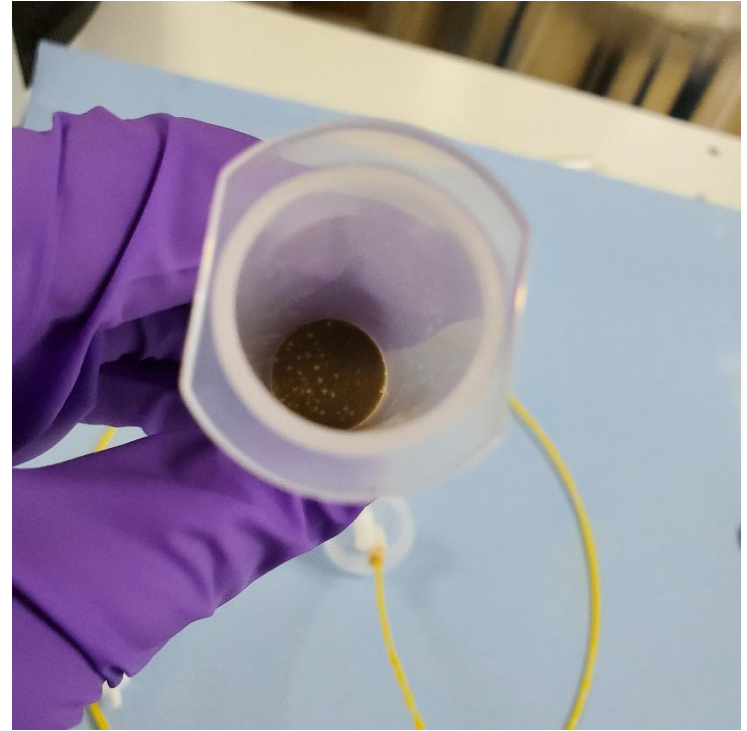
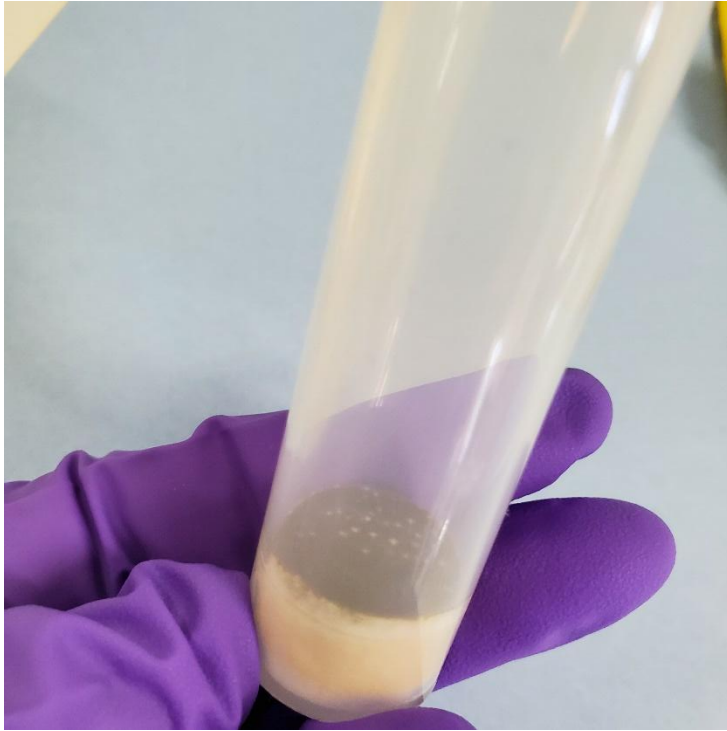
6ml and 25ml Cartridges



250 ml run to completion on 6 ml cartridge with Plastic Wool

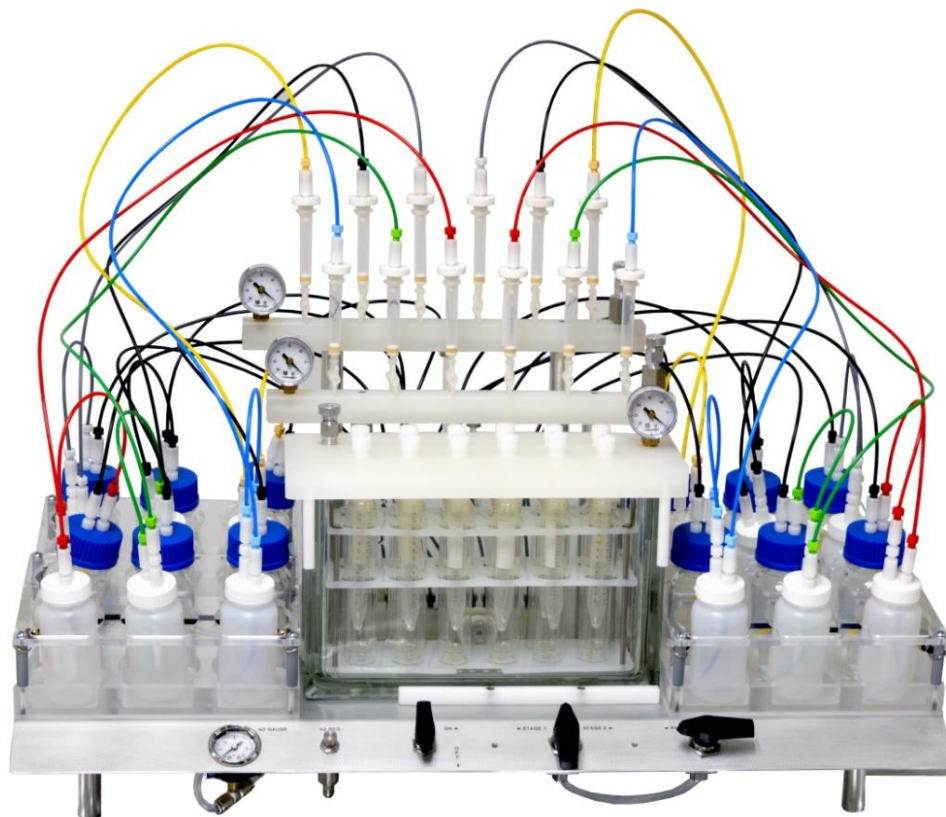


250ml run to completion 25ml cartridge



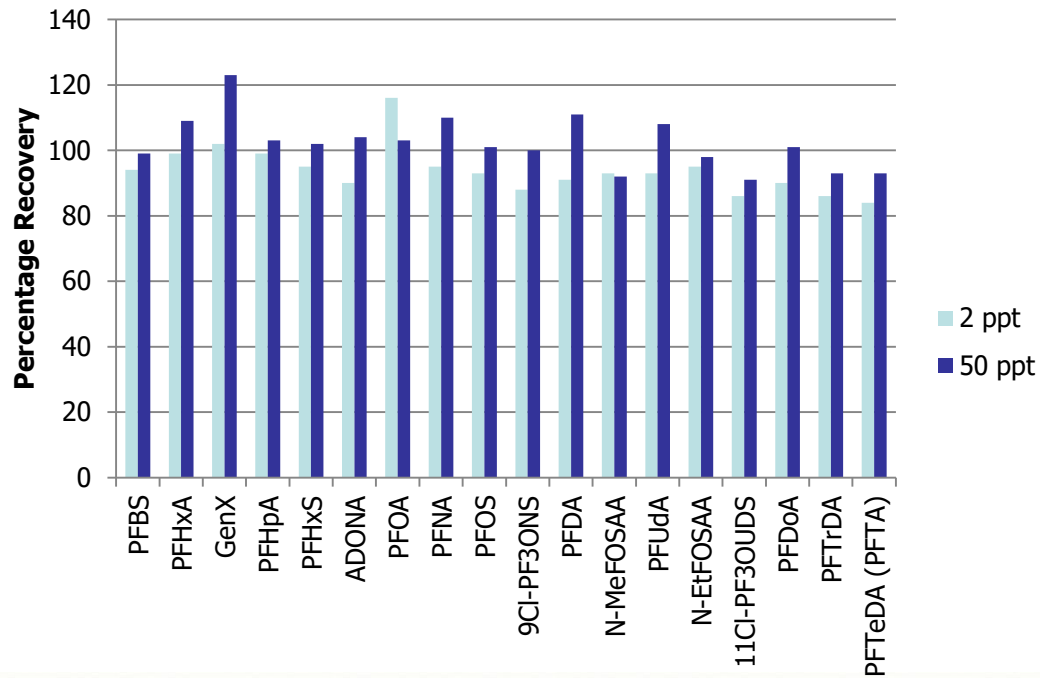
Clean up is easy with no cross contamination

- Back Flush the sample line into the original sample bottle with an IPA non-Teflon squirt bottle.
- Wash the inside of the bottle cap with IPA squirt bottle
- Wash Cartridge Adapters with IPA squirt bottle or sonicate in a beaker
- Ready for the next 12 samples

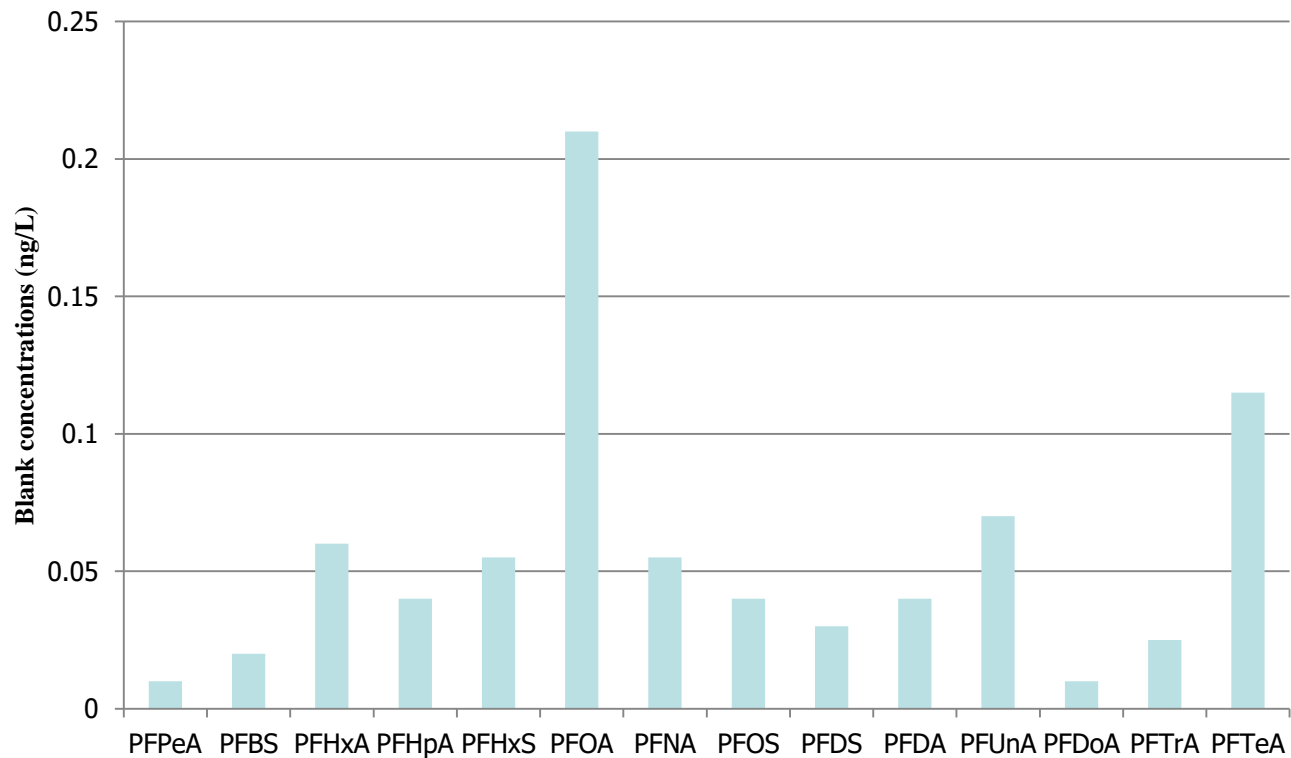


EZPFC 12 Sample System

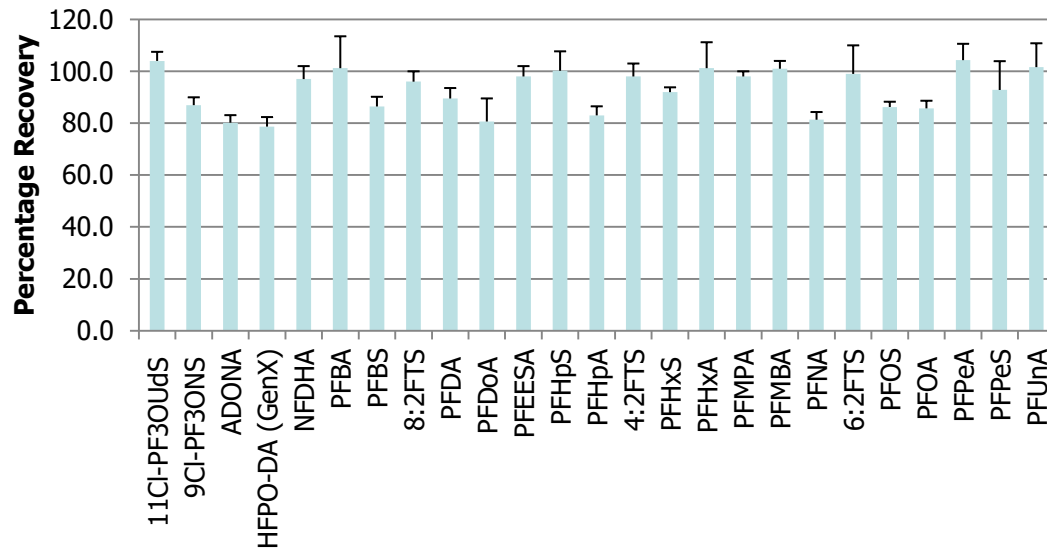
EPA 537.1



PFAS Background



EPA 533



- **EZPFC and SuperVap systems are easy to use and install**
 - Complete Water Sample Prep Workflow
- **Low cost, High throughput, Low maintenance solution**
- **EZPFC Extractions and Concentration**
 - Closed System Reduces Contamination
 - Reduces Human error



Summary

- **FMS semi-automated SPE and SuperVap systems deliver consistent, reproducible results**
- **Handles a wide range of Sample sizes and matrix types**
- **Uses all SPE Cartridge sizes**
- **Comply with existing methods that require vacuum, positive pressure and precise delivery of sample and solvents**



Summary

- **New Solid Phase Extraction Chemistries and Methods are continuously being developed**
- **EZPFC**
 - Designed for Semi-Automated PFAS Extractions
 - SuperVap PFC Concentrator for 24 samples
- **Capable of performing in line extract drying and/or Cartridge extract clean-ups**

